Model Systems for Iron and Copper Containing Oxygenases

Lubben, Marcel; Schudde, Ebe P.; Wilkinson, Elizabeth C.; Que, Jr.; Hermant, Roel; Hage, Ronald; Feringa, Bernard

Published in:
Journal of Inorganic Biochemistry

DOI:
10.1016/0162-0134(95)97786-P

N43 MODEL SYSTEMS FOR IRON AND COPPER CONTAINING OXYGENASES

Ben L. Feringa[a], Marcel Lubben[a], Ebe P. Schudde[a], Elizabeth C. Wilkinson[b], Lawrence Que, Jr.[b], Roel Hermant[c] and Ronald Hage[c]

[a.] Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. [b.] Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A. [c.] Unilever Research Laboratories, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands.

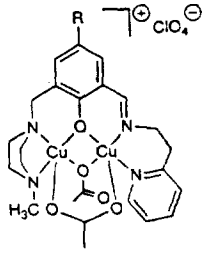
The activation of dioxygen in biological systems and the selective oxygenation of arenes, alkanes and alkenes is a challenging area of research. Recent emphasis is on functional modeling of metaloxygenases to unravel molecular mechanisms of catalysis and on the design of new catalysts for oxygen atom transfer.[1] Structural and functional models for mono- and dinuclear metalloenzymes as well as new oxidation catalysts[2] will be presented.

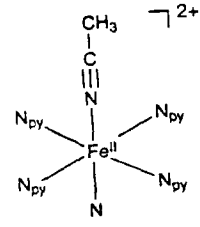
New methodology for multidentate ligands, based on sequential aromatic Mannich reactions, allows the formation of non-symmetric dinuclear complexes,[3] mimicking aspects of the binding of metal ions of dinuclear metalloenzymes (such as tyrosinase) in different environments.

The synthesis, structures and properties of non-symmetric dinuclear Cu(II)-complexes (e.g.1) with chemically or geometrically distinct copper-centers are described.[4] The stepwise complexation of Cu(II) was determined by microcalorimetry. The molecular structure of a related dinuclear Fe(III) complex was also elucidated.

Our focus in mononuclear iron-oxygenase mimics is on nonheme iron centers in oxygen activation.

The synthesis and X-ray structure of the low-spin iron (II) complex $[Fe(N_4py)CH_3CN](ClO_4)_2$ (**2**) of the new pentadentate ligand N_4py is reported. The complex reacts with hydrogen peroxide at room temperature to form a transient purple species, which exhibits low-spin Fe(III) EPR signals similar to those of activated bleomycin. The intermediate is formulated as an iron(III)hydroperoxide. Spectroscopy and catalytic activity in hydrocarbon oxidations are described.





1. Bioinorganic Catalysis" J. Reedijk, ed., Marcel Dekker Inc., New York, 1993.
2. B.L. Feringa, O.J. Gelling, M.T. Rispens, M. Lubben, in "Transition Metals in Supramolecular Chemistry", L. Fabrizzi ed., Nato-ASI; Kluwer 1994, 171-190.
3. M. Lubben, B.L. Feringa, J. Org. Chem. *59*, 2227, **1994**.
4. M. Lubben, R. Hage, A. Meetsma, K. Bijma, B.L. Feringa, Inorg. Chem. 1995, in press.